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ON ION-INDUCED NEW-PARTICLE FORMATION: FROM WELL-DEFINED LABORATORY EXPERIMENTS TO ATMOSPHERIC OBSERVATIONS

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Academic dissertation

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On ion-induced new-particle formation: from well-defined laboratory experiments to atmospheric observations

Robert Leopold Rudolf Wagner

University of Helsinki, 2017

Abstract

Aerosol particles can be directly emitted to the atmosphere in many ways, such as sea spray, volcanoes, wildfires or industrial combustion processes. However, aerosol particles also form in the atmosphere, when precursor gases nucleate and new-particle formation occurs. This phenomenon is frequently observed in the atmosphere, and studies suggest that approximately half of the global budget of cloud condensation nuclei results from secondary particle formation. Nevertheless, we do not yet understand atmospheric new-particle formation in detail.

This thesis addresses underlying processes of new-particle formation in the atmosphere, with focus on the role of ions in those processes. The aim is to increase the understanding on atmospheric processes and the interpretation of observations, which are crucial to improve climate change predictions.

Organic vapors with very low volatilities were found to play a significant role in both nucleation and growth of molecular clusters. These vapors can form through oxidation of volatile organic compounds such as monoterpenes (e.g. alpha-pinene or delta-3-carene, $C_{10}H_{16}$). While for a long time the prevailing opinion was that nucleation does not occur without sulfuric acid as a precursor, we found that organic vapors with very low volatilities can form particles even in the absence of sulfuric acid. Moreover, the early growth of freshly formed clusters can also be governed by low volatility organics.

In cases where conditions are unfavorable for neutral clusters to form, ions can help by stabilizing nuclei, thus facilitating new-particle formation (ion-induced nucleation). To be able to study ion-related effects in detail, accurate ion concentration and size measurements are vital. For this thesis, we performed calibration measurements to verify the output of the neutral cluster and air ion spectrometer. We identified deviations in ion concentrations of up to 30%. By applying the correction terms that we derived from our laboratory results, the uncertainty of measured ion concentrations can be reduced to 10%.

Studying the effect of ions on new-particle formation, we found that the contribution of ion-induced nucleation is sensitive to the concentration of cluster ions, decreasing towards low concentrations. High concentrations of cluster ions indicate small sinks of ions and charged clusters, as well as high recombination rates. The difference in cluster ion concentrations between the boreal forest in Hyytiälä, Finland, and the laboratory environment at CERN, Switzerland, can, at least partly, explain the different contributions of ion-induced nucleation when comparing results from the two environments.

This thesis addresses new-particle formation, especially nucleation and growth processes, and provides new insights to the participating precursor gases and the role of ions. Linking laboratory studies to ambient observations is challenging, and further investigation is needed to confirm implications for the Earth's atmosphere.

Keywords: new-particle formation, ions, aerosol-ion interactions, CLOUD, chamber, nucleation, HOM, NAIS, PSM

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This thesis consists of an introductory review, followed by five research articles. In the introductory part, the publications are cited according to their roman numerals. **Paper I** is reproduced with permission of the Boreal Environment Research Publishing Board. **Paper II** is reproduced with permission of Elsevier (license no. 4197780760395). **Papers III–V** are reprinted under the Creative Commons Attribution 4.0 International (CC BY 4.0) license.

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1 Introduction

An aerosol is solid or liquid particles suspended in air. We are surrounded by aerosol particles at all times. Their concentrations may vary from a few particles per cubic centimeter in the arctic (e.g. Kyrö et al., 2013), up to a million per cubic centimeter in polluted urban environments. Aerosol particles and their health effects received much attention after dramatic smog events. One example is the smog period in London in December 1952, when aerosol loadings were extremely high, visibility decreased to about 50 cm, and approximately 4000 people died prematurely. This incident increased the awareness, and clean air acts were passed in the government few years later. To this day, aerosol particles pose a threat to our health in regions with high emissions, such as metropoles in China or India. Studies suggest that in the year 2000, emissions from China alone could be associated with the premature death of half a million people due to aerosol related health problems (Saikawa et al., 2009). More recent results indicate that even 2.5 million people die in China each year as a consequence of indoor and outdoor air pollution (Kulmala, 2015). Moreover, it was observed that the occurrence of lung cancer has increased dramatically, in heavily polluted environments (Tie et al., 2009).

In contrast, the existence of aerosol particles is critical for our climate and environment as we know it today. Without aerosol particles, clouds could not form and the water cycle, which brings life to land surfaces, would not exist. Another aerosol effect, which is currently often discussed, is the influence on Earth's climate. Aerosol particles directly influence the radiative forcing of the atmosphere by scattering and absorbing sunlight, as well as indirectly by influencing the brightness and life time of clouds, when acting as cloud condensation nuclei (Albrecht, 1989). Except for black carbon particles, aerosol particles are thought to cool the atmosphere through scattering as well as through cloud adjustments, since clouds appear brighter when an increased number of cloud condensation nuclei is present, and thus reflect more sunlight. Overall, aerosol particles are thought to cool the atmosphere, however, those estimations are very uncertain. Especially the cooling effect of cloud adjustments due to aerosols still has large error bars (IPCC, 2013), and contributes significantly to the uncertainty of the total radiative forcing.

Sources of aerosol particles are manifold. They are directly emitted from natural sources such as volcanoes, sea spray, mineral dust, and anthropogenic sources like industrial combustion processes. Depending on meteorological conditions and particle size, aerosol particles can travel over long distances. The calculation of air mass back trajectories helps in understanding transport phenomena. Moreover, aerosol particles form from precursor vapors in the atmosphere through gas-to-particle conversion (Kulmala et al., 2014). This phenomenon is frequently observed in the atmosphere, on roughly 30% of the days in the boreal forest in Hyytiälä, southern Finland (Dal Maso et al., 2005), and also in more polluted urban environments (McMurry et al., 2005). New-particle formation (NPF) is thought to contribute about 50% to the global budget of cloud condensation nuclei (CCN; Merikanto et al., 2009), even in a polluted urban environment (Kulmala et al., 2016). Hence, to be able to

understand and predict climate changes due to aerosol particles, it is vital to increase our understanding of formation processes of secondary particles.

The first steps of new-particle formation are chemical reactions in the gas phase, which lead to the formation of compounds with low volatility (Kulmala et al., 2014). Those compounds enable clustering and subsequently nucleation, e.g. when a molecular cluster is formed from precursor gases such as sulfuric acid or ammonia together with water. The existence of charged clusters can be observed (e.g. Hõrrak et al., 1998; Arnold, 1980), whereas the detection of neutral clusters is problematic, however, secondary observations as well as model results suggest high concentrations of neutral clusters (Kulmala et al., 2005). From there, the fate of the clusters depends on many factors. It is possible that the newly formed cluster is relatively unstable and breaks apart again. Otherwise, the clusters can easily be lost onto the surface of pre-existing aerosol. For the molecular cluster to survive, it has to grow by condensation to reduce its diffusivity, and hence reduce the likelihood to be lost onto the surface of another particle. The processes described result in a competition: nucleation and growth versus disintegration and coagulation loss. While the coagulation loss to pre-existing aerosol particles can be calculated with good confidence, the other processes are more complex and thus more difficult to describe.

New-particle formation processes can be influenced by ions, which are ubiquitous in the Earth's atmosphere. They form through collisions of energetic particles with molecules in the atmosphere (mostly oxygen and nitrogen), or through other charge separation mechanisms such as friction charging or splashing of water (balloelectric ions, Lenard effect). Particles with high enough energy for ionization originate from cosmic or radioactive radiation. Radioactive decay of Radon that is available in soil in certain areas, as well as fallout from the Chernobyl accident significantly influence ion concentrations (Hõrrak et al., 1994). High ion concentrations were also observed near waterfalls (Laakso et al., 2007b), during rain fall (Hõrrak et al., 2006), at high wind speeds (e.g. Hõrrak et al., 1998), and in combustion engine exhausts (e.g. Haverkamp et al., 2004). Sinks for air ions are manifold surfaces such as plants (Tammet, 2006) or larger aerosol particles, as well as cloud and fog droplets. Depending on ambient conditions, the resulting concentration of small ions in the mobility range 3.6–0.6 $cm^2\ s^{-1}\ V^{-1}$ may vary between <100 – 4000 cm^{-3} per polarity (Hirsikko et al., 2011; Hõrrak, 2001). Their chemical composition depends on available trace gases, since after an ion pair has formed, the negative charge attaches to compounds with the lowest proton affinity, the positive charge to compounds with the highest proton affinity. According to Arnold et al. (1978) stratospheric ions can be divided into proton hydrates and non-proton hydrates, and negative ions are thought to contain inorganic acids (Arnold, 2008). In the upper troposphere at a height of 9–10 km above ground, proton-hydrates, and clusters involving acetone and sulfuric acid were observed (Eichkorn et al., 2002). At ground level, negative ions are dominated by inorganic acids; amines, pyrodines, and quinolines were among the most abundant positive ions (Eisele, 1989a, b; Luts and Salm, 1994; Parts and Luts, 2004; Junninen et al., 2010; Ehn et al., 2010). In the literature ions are often categorized according to Hõrrak et al. (2000) in small (<1.6 nm), intermediate (1.6–7.4 nm), and large ions (7.4–20 nm). While there is no clear border line between ions and charged aerosol

particles, intermediate and especially large ions can already be regarded as charged particles.

To study nucleation and growth processes and the effect of ions in great detail, an accurate measurement of ion sizes and concentrations is crucial. An instrument that is widely used to measure ion spectra is the neutral cluster and air ion spectrometer (NAIS). The performance of the NAIS was verified in earlier studies. Asmi et al. (2009) compared ten ion spectrometers (5 NAIS; 5 AIS – air ion spectrometer – which is an earlier version of the instrument) and a balanced scanning mobility analyzer (BSMA), confirming that the NAIS works well overall. However, ion mobilities were overestimated by up to 40% and ion concentrations were overestimated when low concentrations were measured. In a follow-up experiment, an intercomparison workshop of eleven ion spectrometers (6 NAIS, 5 AIS), the general agreement was still good, but ion concentrations were again too high and background noise was identified as the main error source (Gagne et al., 2011). Both studies highlighted the importance of the data inversion algorithm, a mathematical model that is used to convert the measured spectra of electrometer currents to ion number-size distributions (Mirme and Mirme, 2013). This thesis eventually addresses inconsistencies in data inversion, to assess the accuracy of the output of the instrument when measuring ions and naturally charged aerosol (**Paper I**).

Atmospheric observations of NPF both at urban locations (e.g. Alam et al., 2003; Dunn et al., 2004; Wu et al., 2007; Salma et al., 2011; Dall'Osto et al., 2013) and in remote environments (e.g. Dal Maso et al., 2005; Boulon et al., 2010; Pierce et al., 2014) often demonstrate similar characteristics, namely a seasonal cycle driven by solar radiation and the abundance of precursor vapors, and a dependence on pre-existing particle concentrations. The dependence on solar radiation illustrates in influence of photochemistry, since ultra-violet (UV) radiation is necessary to form the hydroxyl radical (OH), which is one of the most important oxidants in the atmosphere. The abundance of precursor vapors, as well as the aerosol concentration, can strongly depend on the origin of the air masses at a given location. We investigated seasonal effects in NPF in an urban environment in Vienna, Austria, and investigated the possible influence of the air mass origin (see Sect. 7 for details, **Paper II**).

The atmosphere is a very convoluted system, and drawing conclusions is often tricky. Therefore, laboratory experiments with simpler and well-defined structure are conducted to complement atmospheric observations. The Cosmics Leaving OUtdoor Droplets (CLOUD; Kirkby et al., 2011; Duplissy et al., 2016) chamber experiment at the European organization for nuclear research (CERN), Switzerland, is dedicated to investigate nucleation processes in great detail. Since contamination levels are extremely low, trace gases that may participate in nucleation processes can be studied selectively. To enable studying the effect of ions, the chamber is built from conductive material only and, moreover, the CERN proton synchrotron (PS) can be used to simulate ionization rates higher up in the atmosphere. Hence, the CLOUD chamber is a highly sophisticated facility to study nucleation and growth processes, and the influence of ions. However, as the chamber environment is a very simplified version of the Earth's atmosphere, conclusions for processes under actual atmospheric conditions need to be considered carefully. Nonetheless, new theories can often be tested in a

laboratory only. In this way, atmospheric and laboratory studies can support each other and deeper understanding can be achieved. The results of **Paper III–V** are based on measurements conducted at the CLOUD chamber.

While earlier studies reveal that sulfuric acid is very important in nucleation processes (Kuang et al., 2008; Kulmala et al., 2013), atmospheric concentrations are typically too low ($[H_2SO_4] \approx 10^5$–10^7 cm^{-3}) to explain the observed nucleation rates through sulfuric acid and water alone (Kirkby et al., 2011). It has been discovered that volatile organic compounds (VOCs) can form vapors with very low volatilities through oxidation (Kulmala et al., 1998; Ehn et al., 2014), which are thought to influence both nucleation and growth processes. Earlier studies already pointed toward the participation of organic vapors in particle growth (e.g. Hirsikko et al., 2005). In this thesis, we confirm that organic vapors with very low volatilities can play an important role in nucleation processes (**Paper III**) and the subsequent cluster growth (**Paper IV**).

Since charged molecular clusters show enhanced stability (Yu and Turco, 2001), ions can assist in nucleation processes (ion-induced nucleation), and thereby enhance the production of cloud condensation nuclei. The formation and growth of charged particles is frequently observed in the atmosphere (e.g. Hirsikko et al., 2007). Therefore, cosmic ray intensity and cloud cover could be linked (Carslaw et al., 2002), however, no correlation between cosmic ray ionization intensity and new-particle formation was observed at the boreal forest in southern Finland (Kulmala et al., 2010). The significance of ion-induced nucleation in cold environments such as in the middle or upper troposphere, as well as its minor importance in the boundary layer was already indicated by laboratory studies conducted by Lovejoy et al. (2004) and Curtius et al. (2006). Ambient measurements demonstrate little significance of ion-induced nucleation in the boundary layer (Iida et al., 2006; Gagne et al., 2008; Kontkanen et al., 2013; Kulmala et al., 2010; Kulmala et al., 2013; Manninen et al., 2010; Manninen et al., 2009; Laakso et al., 2007a). In contrast, a considerable contribution of ion-induced nucleation to the global tropospheric aerosol is predicted by some model calculations (Kazil et al., 2010; Yu et al., 2010). A detailed review of observations is provided by Hirsikko et al. (2011). Since galactic cosmic ray (GCR) ionization is an important source of ions in the atmosphere, a mechanism that links GCR ionization to cloud properties cannot be excluded (Harrison and Carslaw, 2003; Kazil et al., 2008). Increasing the understanding how ions influence nucleation processes is one aim of this thesis, and our findings are discussed in detail in Sect. 9 (**Paper V**). A schematic drawing of the most important steps in the formation of secondary aerosol particles is displayed in Figure 1.

Main objectives of this study:

(i) Conduct a laboratory calibration to enable the accurate measurement of the size and concentration of ion clusters with the neutral cluster and air ion spectrometer.

(ii) Quantify the contribution of low-volatility organic vapors to nucleation and subsequent growth of organic particles.

(iii) Confirm and further explore the role of ions in new-particle formation, and investigate reasons for the discrepancy between ambient and laboratory experiments from CLOUD and SMEAR II.

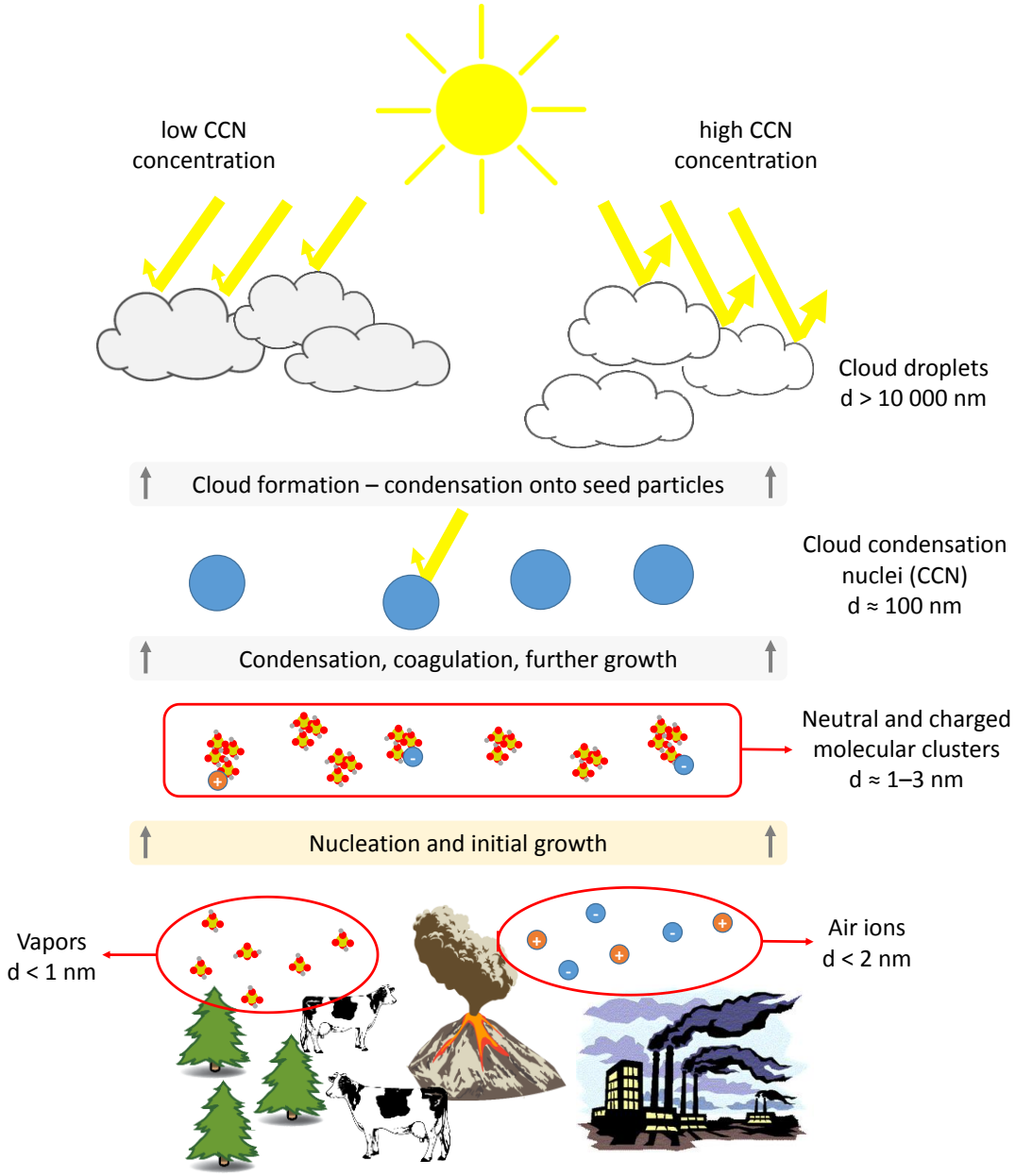

Figure 1. Schematic drawing illustrating the most important steps from new-particle formation to cloud droplets. Approximate diameters are represented by the variable *d*. Circled areas are studied in this thesis.

2 Theory and definitions

Many terms used in this thesis are referred to as 'text book knowledge'. However, we are doing research in a dynamic field, definitions may change and terms alter. Therefore, topics most important for this thesis are discussed below.

New-particle formation is frequently observed in the atmosphere for many years by now. As we started to understand the phenomenon better and better, the term 'new-particle formation' was widened to include all related processes. New-particle formation starts with the formation of extremely low- and low-volatile compounds through chemical reactions (oxidation processes; Kulmala et al., 2014). Extremely low-volatile compounds can cluster with each other, or with other molecules to form stable clusters; in the case that an energy-barrier was overcome, this process is called nucleation. Low-volatile compounds then condense on the formed clusters together with extremely low-volatile compounds. As the newly formed particle grows in size, also more volatile compounds can participate in condensational growth.

An important parameter when studying new-particle formation is the **nucleation rate**, which is mostly represented by the variable *J*. The nucleation rate measures the rate at which thermodynamically stable clusters are formed (cm^{-3} s^{-1}). The critical size at which particles are considered thermodynamically stable is usually estimated around a diameter of 1.5 nm. When observing the rate of particles appearing at sizes larger than the critical diameter, *formation* rates are reported.

Once a particle has formed, depending on ambient conditions, it can further grow in size. The particle **growth rate** measures the rate at which the particle diameter increases (GR; nm h^{-1}), and can be decisive for the fate of a newly formed particle. If a particle grows fast, its diffusivity, and thus its likelihood to be lost onto the surface of pre-existing particles, decreases fast.

When measuring the diameter of small aerosol particles, technically, their **electrical mobility** is determined and then converted to the mobility equivalent diameter (Millikan conversion; Mäkelä et al., 1996). A more advanced mobility-diameter conversion is described by Tammet (1995). The electrical mobility is a term which originates from the *mechanical* mobility (Hinds, 1999), which describes the ability of a particle to move through air and can be written as

$$B = \frac{V}{F_D} = \frac{C_c}{3\pi\eta d}, \quad (1)$$

where V is the velocity of the particle, F_D the resisting force according to Stokes' law, and C_c the Cunningham slip correction factor which corrects the resisting force for particles smaller than about 1 μm in diameter where the surrounding air cannot be treated as continuum anymore. The electrical mobility (Hinds, 1999) describes the ability of a particle to move through an electrical field and can be written as

$$Z = neB, \quad (2)$$

where *n* is the number of elementary charges carried by the particle, *e* the elementary charge, and *B* the mechanical mobility (1).

The electrical mobility of aerosol particles can be determined via **differential mobility analysis**. When number-size distributions shall be determined, charge equilibrium of the aerosol sample needs to be established. This is mostly done by using a bi-polar radioactive charger (e.g. ^{241}Am). Subsequently, the aerosol is lead into a capacitor, where they are dragged to the other electrode by the electrical field according to their electrical mobility. By varying the voltage that is applied to the capacitor, the particles can be separated in mobility bins and finally the number size distribution of the aerosol can be determined. The method is described in detail by Wang and Flagan (1990).

The **volatility** is a measure of the tendency of a substance to vaporize. When describing the volatility of a chemical compound, often the saturation mass concentration *C** is reported. This quantity is analogous to the saturation vapor pressure, only C* does not represent a pressure, but a mass concentration (µg m^{-3}) at which condensed phases and gas phase are at equilibrium. However, in aerosol physics we usually report saturation vapor concentrations in the unit molecules per cubic centimeter.

When studying the influence of ions on NPF processes, an important observable parameter is the concentration of small ions, which are essentially singly charged molecular clusters. Therefore, the term **cluster ions** is used in this thesis to describe ions in the mobility range 3.6–0.6 cm^2 s^{-1} V^{-1}, which translates to a mobility equivalent diameter of about 0.75–1.8 nm (Millikan-Fuchs conversion; Eq. 2).

3 Methods

3.1 Measurement facilities

3.1.1 CERN CLOUD (Cosmics Leaving OUtdoor Droplets) experiment

The CLOUD experiment is located at CERN in Geneva, Switzerland. It operates a chamber, which is used to simulate atmospheric processes. The focus of the experiment is nucleation and new-particle formation, however, cloud microphysics and chemistry can be investigated as well.

The CLOUD chamber is a stainless steel cylinder of about 3 m diameter and a volume of 26.1 m^3. Its inner surfaces are electropolished to minimize the influence of contaminants. In preparation of a measurement campaign, the chamber is rinsed with ultra-pure water and subsequently heated to 373 K. While cooling down to operation temperature (e.g. 278 K), the chamber is flushed with humidified ultra-pure synthetic air, containing several ppbv of ozone. By applying this procedure, extremely low contaminant levels are achieved, which enable the study of clean conditions such as pristine, pre-industrial environments. Experimental precursor gas concentrations can be carefully adjusted by using a sophisticated gas supply system. Several light sources are installed to initiate photochemistry: 4×200W Hg-Xe (250–450 nm; Kupc et al., 2011), 3 W KrF excimer laser (248 nm), and a so-called UV-sabre (400 W, 385 nm).

The chamber is built entirely from conductive materials to enable studying ion-related processes. While ions in the chamber are constantly produced by galactic cosmic rays (GCR), the ion concentrations can be enhanced by using the CERN proton synchrotron pion beam (3.5 GeV/c). This way, different ionization rates can be studied that resemble the atmosphere from ground level up to about 15 km altitude. Moreover, when the effect of ions shall be excluded, ion-free conditions can be established by using a high voltage field cage, which is installed inside the chamber. When switched on, the resulting field intensity is 20 kV/m, which scavenges ions very efficiently. The chamber setup is described in detail by Kirkby et al. (2011), and Duplissy et al. (2016).

3.1.2 Station for Measuring Ecosystem-Atmosphere Relations (SMEAR II)

The SMEAR II station is located in Hyytiälä, southern Finland. It is situated at an altitude of 181 m a.s.l. in a fairly homogeneous pine forest. As the name of the station suggests, soil-forest-atmosphere interactions are investigated. Moreover, SMEAR II was one of the first measurement sites to observe atmospheric new-particle formation. Many parameters such as chemical composition of the gas phase and bulk chemical composition, aerosol and ion number-size distributions, cloud cover, solar irradiation, as well as gas fluxes and meteorological data are measured continuously throughout the year. Thus, the station provides com-

prehensive information to study new-particle formation and produced the longest continuous measurement of aerosol number-size distributions ever recorded (>20 years; from 1996 onwards). The SMEAR II station and its philosophy are described in detail by Hari and Kulmala (2005).

3.1.3 Vienna roof top laboratory

The Central European city Vienna, Austria, is located 210 m a.s.l. and has a population of around 1.9 million people. The laboratory is situated on top of the physics building in central Vienna, strongly influenced by traffic emissions. At a height of 35 m above ground and a distance of about 100 m to the nearest busy road, it can be considered as an urban background location, and the detected aerosol is well-mixed. The measurement site is described in more detail by Hitzenberger et al. (2006) and Reisinger et al. (2008).

Among other instruments that are installed at this measurement site, we used the following to obtain the results presented in this study (**Paper II**). A twelve-stage small deposit area cascade impactor (SDI) was used to collect aerosol samples in the range 0.04–13.5 µm aerodynamic diameter for mass size distribution, and chemical composition analysis through ion chromatography. Number size distributions were measured with a differential mobility particle sizer (DMPS) in the range 10–600 nm.

3.2 Instruments

A complete description of all instruments that were necessary to obtain the results presented in this thesis is beyond the scope of the introductory review. Therefore, only key instruments are presented below.

Ion number-size distributions were measured with a **neutral cluster and air ion spectrometer** (NAIS; Mirme and Mirme, 2013), a commonly used aerosol and ion mobility spectrometer, manufactured by Airel Ltd. By operating two cylindrical differential mobility analyzers in parallel, positively and negatively charged particles are classified simultaneously. Ion number size distributions measured with the NAIS are an essential part of this thesis. The NAIS sequentially operates in three modes: ion-, particle-, and offset-mode.

In ion-mode, the instrument classifies ions and naturally charged particles in the mobility diameter (Millikan-Fuchs conversion; Eq. 2) range 0.75–45 nm (Mirme and Mirme, 2013). The sample air enters the analyzers close to the center-electrode, and ions are subsequently drifted by the electric field towards the outer electrodes, where they are deposited on one of the 21 electrometer rings according to their electrical mobility. Accounting for diffusional losses in the instrument and assuming singly charged particles, the resulting spectra of electrometer currents can be inverted to number-size distributions.

When operated in particle-mode, the instrument charges the aerosol sample with ions from corona discharge. In this way, also neutral particles can be detected and the total aerosol can

be classified. The size range in this measurement mode is 2–45 nm, as the corona ions saturate (dominate the signal) the lowest fraction of the mobility spectrum (Manninen et al., 2011).

Offset currents of the electrometers are measured in offset-mode. The aerosol is charged in opposite polarity to the subsequent analyzer and an electrical filter is switched on, to ensure that no detectable aerosol can enter the analyzers. The obtained offset currents are then used to correct the measured ion and particle spectra.

The strength of the NAIS is the ability to measure the first steps of nucleation at a high time resolution, as well as its tolerance for high concentrations. However, the background concentration due to electrometer noise limits the possibility to measure concentrations lower than roughly 50 ion pairs per cubic centimeter. The NAIS is described in more technical detail by Mirme and Mirme (2013), and measurement principles are illustrated by Manninen et al. (2016).

In addition to the NAIS, the **cluster ion counter** (CIC; Airel Ltd.; prototype) was used to determine the concentration of small ions. It is an ion counter developed by Airel Ltd., the same company that builds the NAIS, and detects positively and negatively charged ions simultaneously. The CIC consists of two cylindrical analyzers, each equipped with three electrodes. The electrometer currents are determined at a frequency of 30 Hz to detect rapid concentration changes. The analyzers are operated without sheath flow, thus the size information that can be obtained is very crude. All ions with a mobility $z > 2.5$ cm^2 V^{-1} s^{-1} ($d_p <$ 0.9 nm) are deposited on the first electrode, $z > 0.5$ cm^2 V^{-1} s^{-1} ($d_p < 2$ nm) on the second, and $z > 0.25$ cm^2 V^{-1} s^{-1} ($d_p < 2.82$ nm) on the third electrode. Larger ions that enter the analyzer close to the electrodes can be detected as well. The CIC can be operated at flow rates between 10 l min^{-1} and 60 l min^{-1} per analyzer. The instrument is described in more detail by Mirme et al. (2017).

The **particle size magnifier** (PSM; Vanhanen et al., 2011) manufactured by Airmodus Ltd. is used together with a condensation nuclei counter (CPC; McMurry, 2000) as a two-stage nano-particle counter. While the first stage (PSM) activates clusters starting from mobility diameters of roughly 1 nm and grows them to about 90 nm, the second stage (CPC) further grows them to approximately one micrometer, which makes it possible to optically detect and count them.

The strength of this nano-particle counter, besides detecting very small clusters, is the adjustable saturation ratio in the PSM. Supersaturation is achieved by mixing a hot, saturated air flow with the sample flow, and subsequently cooling the mixture. By adjusting the flow of saturated air, the achieved supersaturation and thus the cut-off diameter can be quickly varied between 1–3 nm. When the instrument continuously varies the threshold diameter (scanning mode), number size distributions between minimal and maximal cut-off diameter can be determined (Lehtipalo et al., 2014).

Recently, a new inlet system was developed, which features an ion filter (Kangasluoma et al., 2016), which can be used to remove ions and charged particles from the sample. The filter operates with electrodes at a potential difference of 2.2 kV, generating an electrical field orthogonal to the sample flow. At a flow rate of 2.5 l/min, ions and charged particles smaller than roughly 13 nm mobility diameter are efficiently scavenged. This way, the neutral fraction of small particles can be determined. While the ion filter can be switched on and off periodically to determine charged fractions, another possibility is to operate two nano-particle counters in parallel, where the ion filter is permanently switched on for one of the instruments, and the other constantly detects the total aerosol concentration. Both methods have their advantages and shortcomings. With periodically switching the filter on and off, the same instrument is used for measuring total and neutral particles, excluding the possibility of instrumental differences. However, the time resolution is lower and quick concentration changes can complicate data analysis. When operating two counters in parallel, the time resolution is very good, but two instruments need to be compared in data analysis, which can introduce additional errors.

At CLOUD, the method of two parallel counters (Fig. 2) was chosen to have maximum time resolution, and the condition of the instruments was closely monitored to avoid inconsistencies between the instruments (**Paper V**).

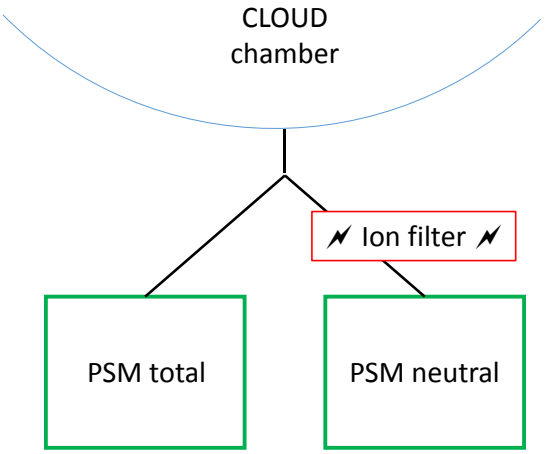

Figure 2. Sampling scheme of the particle size magnifiers at CLOUD.

The two-stage activation method is very efficient to detect nano-particles down to diameters around 1 nm. However, particles of this size are rather molecular clusters, and the chemical composition of the cluster as well as the condensing vapor influences the activation efficiency (Kangasluoma et al., 2014). As a consequence, the cut-off diameter that can be achieved with a certain saturation ratio also varies depending on the composition of the particle. While this behavior can be used to obtain information on the chemical composition of particles (Kulmala et al., 2007a), for this thesis it represented an additional error source.

While aerosol spectrometers characterize the physical properties of particles, **atmospheric pressure interface time of flight (APi-TOF) mass spectrometers** are used to study the

chemical composition of molecular clusters. When studying molecular properties, the clusters first need to be separated from the total aerosol sample. For this purpose, the APi inlet was developed (Eisele and Tanner, 1993), where ions are focused and the pressure is gradually reduced to 10^{-6} mbar. Subsequently, the ions enter the time of flight mass spectrometer, where they are classified according to their mass-to-charge ratio. Together, the instrument forms the so-called APi-TOF (Junninen et al., 2010). By identifying known molecules, the mass scale is calibrated and the mass of unknown molecules can be determined. In many cases, when a distinct molecular configuration is found that matches the mass, also the composition of unknown molecules and clusters can be identified.

When operated together with a chemical ionization inlet (CI-APi-TOF; Jokinen et al., 2012) also neutral clusters can be detected. Depending on the scope of the measurement, different ions can be used to charge the sample molecules. A commonly used ion is nitrate (NO_3^-), which efficiently clusters with organic species, and was used in **Paper III–V** for the detection of highly oxidized organic compounds as well as sulfuric acid. Those primary ions are formed by X-ray ionization of nitric acid in a carrier flow of nitrogen. The generated ions then interact with the sample molecules in an ion drift tube, charging neutral molecules and clusters. After this procedure, the sample enters the APi inlet and the procedure continues as described above. The instrument is described in more detail by Jokinen et al. (2012).

The (CI-)APi-TOF provides the unique opportunity to investigate the chemical composition of gases as well as molecular clusters. This way, the instrument already helped answering many questions when it comes to identifying key precursor vapors for nucleation processes. However, since the transmission efficiency is not easy to determine, measuring absolute concentrations still remains challenging and uncertainties are often around a factor of two or higher.

3.3 Calculation of nucleation rates and growth rates

When calculating nucleation rates, the formation rate of thermodynamically stable clusters shall be determined. **In the atmosphere** usually the concentration change in a size bin (e.g. from NAIS) is observed, including the corrections for particles growing out of the size range as well as coagulation losses. The equation for the formation rate of 2 nm particles can be written as described by Kulmala et al. (2007b)

$$J_2 = \frac{dN_{2-3}}{dt} + CoagS_{2-3} \cdot N_{2-3} + \frac{f}{1\ nm} GR_3 \cdot N_{2-3}\ , \quad (3)$$

where f is the fraction of particles that are activated for growth (often assumed to be unity) and n_3, the concentration of 3 nm particles, is approximated by $N_{2\text{-}3}$/(3 nm - 2 nm), and the coagulation losses are determined according to Seinfeld and Pandis (2016).

To obtain the ion-induced particle formation rate, ion-ion recombination as well as charging of neutral particles need to be considered (Manninen et al., 2009):

$$J_2^{\pm} = \frac{dN_{2-3}^{\pm}}{dt} + CoagS_{2-3} \cdot N_{2-3}^{\pm} + \frac{f}{1\ nm} GR_3 \cdot N_{2-3}^{\pm} + \alpha \cdot N_{2-3}^{\pm} N_{<3}^{\mp} - \beta \cdot N_{2-3} N_{<2}^{\pm}\ , \quad (4)$$

where α is the ion-ion recombination coefficient, and β the ion-neutral attachment coefficient (see e.g. Tammet and Kulmala, 2005).

From measurements **in the CLOUD chamber**, particle nucleation and formation rates can be calculated by studying the changes in total particle concentrations (N_{tot}), and, as for atmospheric measurements, taking into account particle loss parameters (Kirkby et al., 2011; Almeida et al., 2013). Since the instruments constantly sample from the chamber, the removed air needs to be substituted, resulting in artificially lowered concentrations due to dilution (S_{dil}). The chamber is a finite volume where walls have an effect and diffusional losses to chamber walls have to be considered (S_{wall}). When particles are formed and grown, they act as additional surface and small clusters can be lost onto it, leading to a coagulational loss (S_{coag}). Finally, the nucleation rate can be written as (see **Paper V** for details):

$$J = \frac{dN_{tot}}{dt} + S_{dil} + S_{wall} + S_{coag} \quad (5)$$

When investigating ion-effects on new-particle formation, the total particle formation rate J_{tot} can be separated into three different fractions:

$$J_{tot} = J_n + J_{rec} + J_{\pm} \quad (6)$$

J_n is the formation rate of particles without ions being involved ('neutral'), J_{rec} the formation rate of neutral particles through recombination of oppositely charged clusters, and $J_{\pm}$ is the formation rate of charged particles. The term 'ion-induced nucleation' J_{iin} combines the ion-assisted particle formation rates:

$$J_{iin} = J_{rec} + J_{\pm} \quad (7)$$

By measuring the total particle concentration as well as the neutral fraction of it for both neutral chamber conditions and with ions being present, the fractions of the nucleation rate described in (5) and (6) can directly be estimated (**Paper V**).

Growth rates can be determined from aerosol number-size distributions through different methods, such as leading-edge diameter (Lehtipalo et al., 2014) or mode-fitting (Dal Maso et al., 2005). In this thesis, the leading-edge method was used, where appearance times are calculated for each size bin in the spectrum. Appearance times are defined as the time when the particle concentration in the size bin has reached 50% of its maximum and is assigned to the mean diameter of the size channel. By observing the evolution of diameter versus time and applying a linear fit, the growth rate can be calculated (slope of the fit). For a more detailed description of the method as well as the size ranges for which the growth rates were calculated, see **Paper IV**.

4 Verification of the NAIS ion measurement

Besides accurate flow rates and electric fields, the NAIS relies on knowledge of diffusional losses inside the instrument to be able to invert the measured spectra of electrometer currents to ion number size distributions. The manufacturer provides algorithms to perform said inversion, which are adjusted from time to time, to better represent the actual concentrations.

Since we wanted to investigate the role of ions in new particle formation processes, an accurate measurement of small ions was vital. Therefore, we performed laboratory measurements in Helsinki, to test the concentration and sizing accuracy of the NAIS, when employing five different versions of the data inversion algorithms ('inverters', **Paper I**), the most commonly used version, as well as two older and two newer versions. We used tungsten and ammonium sulfate particles as sample aerosol, and selected certain sizes with differential mobility analyzers (DMA). For the smallest particles, 1–5 nm, a high-resolution Herrmann DMA (Herrmann et al., 2000; Kangasluoma et al., 2016) was used, which selects a sample aerosol with very high grade of monodispersity. For selecting sample aerosol sizes 14–30 nm we used a replica of a Vienna type Hauke DMA (Winklmayr et al., 1991). As a concentration reference, we chose an electrometer (TSI 3068B) for ions in the range 1–5 nm, and a condensation particle counter (TSI 3772) for larger ions (14–30 nm). Since the NAIS samples 54 l min^{-1}, the test aerosol needed to be substantially diluted with dry filtered air. The sample preparation inlets are displayed in Figure 3.

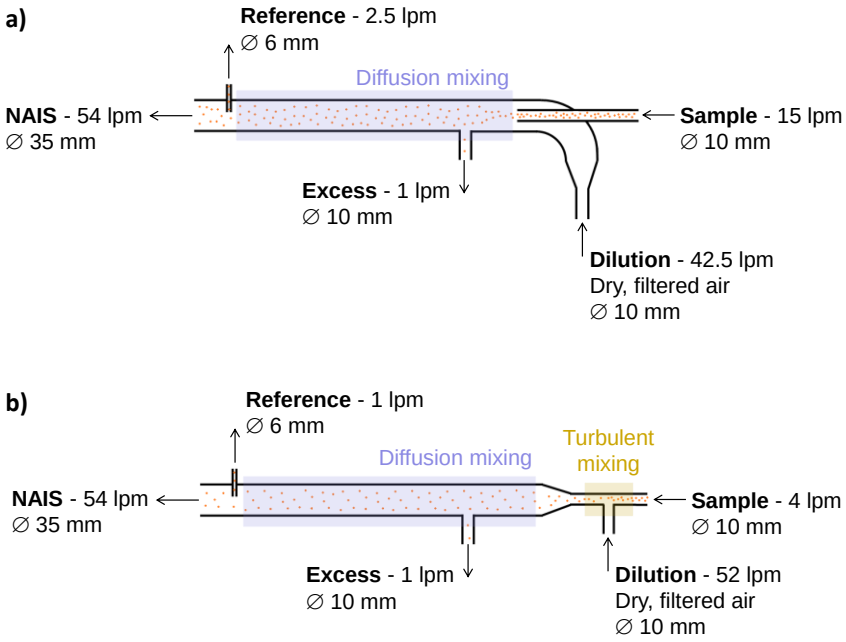

Figure 3. Sample preparation inlets for ions of 1–5 nm mobility diameter (a), and 14–30 nm (b). Differences are in the way how the dilution flow was introduced, as well as in the length of the section for diffusional mixing (a: 50 cm; b: 35 cm; Re = 2153). The figure was adopted from **Paper I**.

We found that the size information provided by the NAIS is very accurate, regardless of the inverter applied for data inversion. In contrast, the concentration values deviated up to 30% from the reference concentrations, and the results were strongly dependent on the version of the inverter. Especially two versions were inconsistent, among them the most commonly used version, 'inv3'. For all other versions of the data inversion algorithm, we could approximate the measured counting efficiencies with a fit, which represents the data very well (Fig. 4). Those functions can be used to correct the measured ion concentrations according their counting efficiencies. By applying the procedures described in **Paper I**, ion concentrations can be determined with the NAIS at an uncertainty lower than 10%.

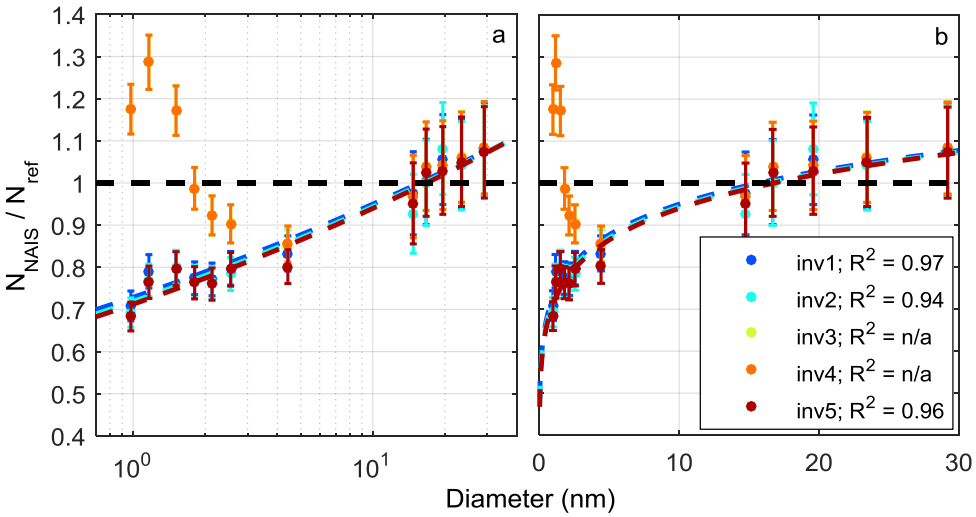

Figure 4. NAIS counting efficiency versus mobility diameter in (a) logarithmic and (b) linear diameter scale. The figure was adopted from **Paper I**.

The correction procedure introduced in **Paper I** is now mentioned in the NAIS operating procedures described by Manninen et al. (2016). Ion concentrations reported in **Paper III–V** were corrected accordingly to achieve highest possible accuracy. Also the ion spectra measured at the SMEAR II station – previous and future – are now by default corrected. Other studies were able to use the calibration results for error estimations (Leino et al., 2016; Kontkanen et al., 2017).

5 Testing the cluster ion counter prototype

The cluster ion counter was used at the CLOUD10 measurement campaign at CERN, Switzerland, in fall 2015 as an additional method to determine the concentration of small ions in the chamber. Noise levels were very low and in general the concentrations compared well to the values determined from the NAIS (Fig. 5).

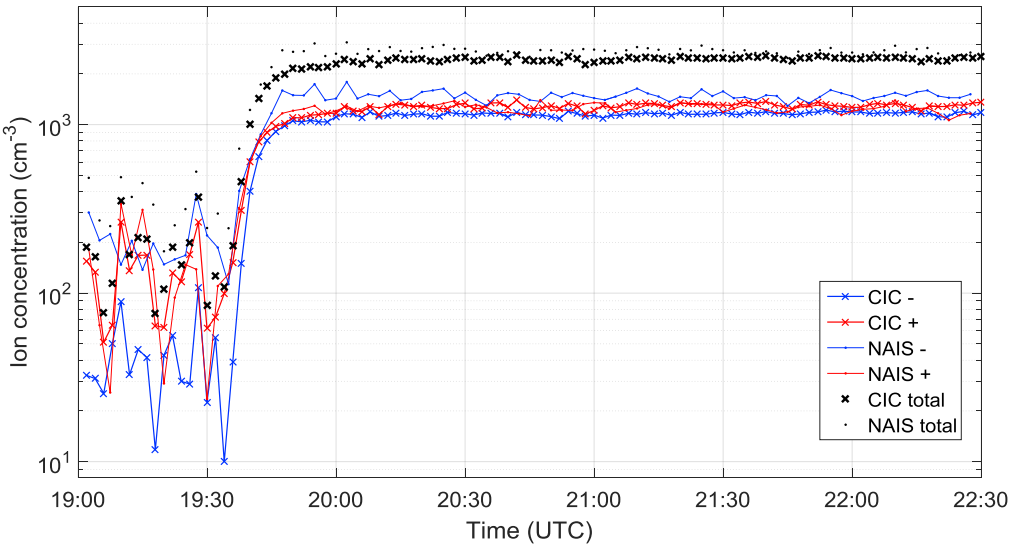

Figure 5. Comparison of cluster ion concentrations measured with CIC and NAIS.

Moreover, the CIC was used to study the wall loss of ions, by adjusting the mixing fan speed in the chamber to different levels while observing the response in ion concentrations (Fig. 6).

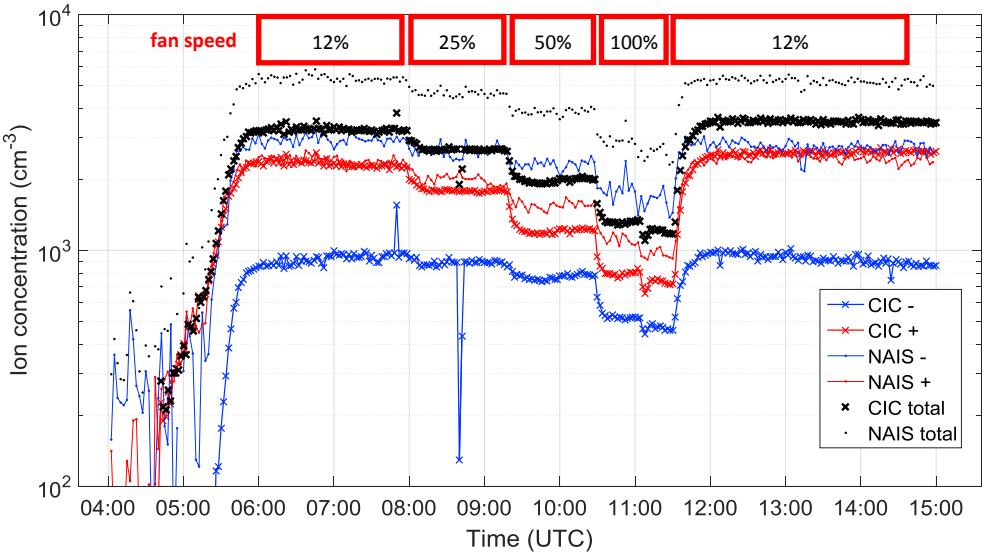

Figure 6. Concentration of cluster ions at various rotation speeds of the mixing fans.

The concentration of cluster ions decreased gradually as the rotation speed of the mixing fans was increased. The CIC underestimated the concentration of negative ions during this run, which was most likely due to an incorrect flow rate. However, the concentration of positive ions was consistent with the concentration values measured with the NAIS.

6 Air ions and ion-induced new-particle formation

In the atmosphere, primary ions form through ionization of air molecules, i.e. collisions of particles from galactic cosmic rays or radioactive decay of unstable isotopes like radon, with nitrogen or oxygen molecules. As a result, N_2^+ and O_2^- are formed, which rapidly transfer their charge through collisions to larger molecules, forming ions such as H_3O^+ and NH_4^+, or NO_3^- and HSO_4^- (Eisele, 1989a; Ehn et al., 2011; Junninen et al., 2010). These ions can attach more molecules, e.g. water, to form larger molecules or molecular clusters, resulting in a ubiquitous population of singly charged small ions, positive and negative, that can be measured with the NAIS (mobility diameter approximately 0.75–1.8 nm, 'cluster ions').

The stability of a molecular cluster increases when it carries a charge (reduced evaporation; Yu and Turco, 2001). As a result, if neutral molecular clusters are unstable, charged clusters have an advantage in the process of new-particle formation. A charged cluster can also overcome the critical size by recombination with an oppositely charged ion. In any case where an ion assists the formation of a thermodynamically stable cluster, the process is called ion-induced nucleation. Earlier studies refer to the same process as ion-mediated nucleation (Yu and Turco, 2001).

Experiments conducted at the CERN CLOUD experiment mostly suggest significant enhancement of nucleation processes through the presence of ions. In a system involving sulfuric acid, ammonia, and water, at nucleation rates lower than the limiting ion-pair production rate of about 4 cm^{-3} s^{-1}, ionization from galactic cosmic rays (GCR) significantly enhanced the nucleation process (Kirkby et al., 2011). Also in a wide range of temperatures resembling the troposphere (249–299 K), particles formed dominantly via ion-induced nucleation pathways in binary and ternary nucleation processes involving sulfuric acid, ammonia, and water (Duplissy et al., 2016). In contrast, it was observed that sulfuric acid, dimethylamine, and water form very stable neutral clusters, thus ion-induced nucleation played only a minor role in this chemical system (Almeida et al., 2013; Kürten et al., 2014). The findings described above are summarized in Table 1. The influence of ions on new-particle formation is discussed in detail in Sect. 9 (**Paper V**).

In polluted environments many vapors are available at high concentrations and the high aerosol load poses an efficient sink for ions and small charged clusters. Thus, the contribution of ion-induced nucleation in urban areas is expected to be minor.

Table 1. Overview of observations concerning ion-enhanced new-particle formation at CLOUD. Abbreviations: MT – monoterpenes; HOMs – highly oxidized organic compounds; J – nucleation rate; IPR – ion pair production rate; T – temperature.

System / Publication	charge-enhancement	limitations
MT ($C_{10}H_{16}$) + H_2O (HOMs, Paper III)	x10 – x100	T = 278 K; [HOM]<1pptv; J < IPR
H_2SO_4 + NH_3 + H_2O (Kirkby et al., 2011)	x2 – x10	T = 248–292 K; J < IPR
H_2SO_4 + H_2O (Duplissy et al., 2016)	negligible	T = 207 K
H_2SO_4 + H_2O (Duplissy et al., 2016)	unclear	T = 223 K
H_2SO_4 + H_2O (Duplissy et al., 2016)	x10	T = 249 K; J < IPR
H_2SO_4 + H_2O (Duplissy et al., 2016)	x100	T = 279 K; J < IPR; predicted by CNT
H_2SO_4 + C_2H_7N + H_2O (Almeida et al., 2013)	minor	T = 278 K

7 Atmospheric observations in an urban environment

Urban air is complex, since many anthropogenic sources add to the chemical composition and availability of trace gases. While a major urban particle source is direct emission, also new-particle formation is significant and frequently observed (e.g. in China: Ahlm et al., 2012; Dall'Osto et al., 2013; Europe: Salma et al., 2011; Salma et al., 2016; Australia: Cheung et al., 2011). However, Puxbaum et al. (2004), found that only 19% of PM2.5 concentrations measured in Vienna, Austria, could be attributed to sources within the city. Therefore, in **Paper II**, we studied the influence of air mass origin on bulk aerosol concentrations, and on the chemical composition of the aerosol.

We analyzed impactor samples from two short-term measurement campaigns, as well as number size distributions from two long-term campaigns. Air mass back trajectories were calculated to obtain the origin of the air masses measured at the roof laboratory on top of the physics building in central Vienna. We used the HYsplit_4 model (Stein et al., 2015) to calculate four trajectories per day for the time window of 72 hours. Depending on directions and wind speeds, Vienna receives continental and marine air masses. However, for some trajectory clusters, the classification marine/continental is ambiguous, due to the complexity of the European coast line (Fig. 7).

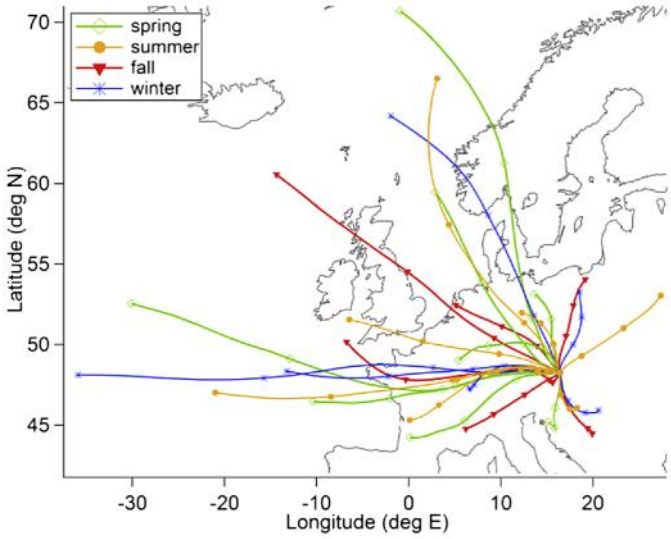

Figure 7. Mean trajectories in clusters divided by seasons. The figure was adopted from **Paper II**.

We found that the chemical composition of coarse particles (d_p > 1.5 µm) was influenced by the origin of the air mass, as we were detecting sea salt related ions (Na^+, Cl^-) with marine air masses, and crustal elements with continental air masses. In contrast, the fine fraction chemical composition was largely independent of the air mass origin, which suggests that the urban fine particle population in Vienna is mostly influenced by regional sources, such

as new particle formation. Similar trends were identified in the region around Toronto, Canada, where five locations (up to 350 km apart) were compared, finding increasing heterogeneity towards smaller particles (Jeong et al., 2010).

We classified number size distributions from two long-term measurement campaigns according to Dal Maso et al. (2005), covering all seasons. On total, NPF events were observed on 12% of all measurement days, most frequently in summer with events occurring on 22% of measurement days. A variety of different NPF frequencies was observed at different urban locations, such as 5% in Birmingham, UK (Alam et al., 2003), 27% in Budapest, Hungary (Salma et al., 2011), or 40% in Beijing, China (Wu et al., 2007). Event start times were mostly between 9 a.m. and 4 p.m., and no NPF events were observed during night time. These observations together with the above average ozone concentrations and solar radiation on days when NPF occurred, underline the importance of photochemistry for nucleation processes. The frequency of new-particle formation was independent of the air mass origin, however, air mass back trajectories (AMBT) are linked to meteorological patterns, which in turn can favor new particle formation. For example, in winter, fast travelling air masses led to low PM2.5 concentrations, sunny conditions and deep mixing layers, and NPF was observed. Local meteorological factors can also influence the concentrations of vapors available for nucleation and condensation.

While our observations suggest a strong influence of photochemistry, we did not determine the chemical composition of the produced vapors, and thus it remains unclear whether the formed vapors were organic or rather sulfuric acid was formed.

8 Simulation of new particle formation at the CERN CLOUD experiment

When trying to understand underlying mechanisms, it is important to simplify the system. At the CLOUD experiment at CERN, systems consisting of few essential vapors are studied, to investigate how they interact, and to identify key parameters driving particle formation and growth processes. **Paper III–V** focus on simulations of the atmosphere, to pursue more elemental understanding of processes related to new-particle formation in the atmosphere.

8.1 Organic vapors with very low volatilities

Organic vapors with very low volatilities are formed through oxidation of volatile organic compounds. This mechanism was further investigated by Ehn et al. (2014), who studied the oxidation products of alpha-pinene (monomer: $C_{10}H_{14–16}O_{7–11}$; dimer: $C_{19–20}H_{28–32}O_{10–18}$). In **Paper III** and **Paper IV**, low volatility organic compounds were further investigated. In these studies, we refer to the term highly-oxidized organic molecules (HOMs), rather than extremely low-volatility organic compounds (ELVOCs), since the analysis of volatilities using the SIMPOL model (Pankow and Asher, 2008) suggests that said molecules spread over a wide range of volatilities (**Paper IV**), from extremely low-volatile to low-volatile, semi-volatile, and even into the range of intermediate-volatile organic compounds with C^* of approximately $10^{2.5}$ μg m^{-3}.

8.2 Nucleation in the absence of sulfuric acid

Sulfuric acid is known to play an important role in atmospheric new-particle formation (Kuang et al., 2008; Kulmala et al., 2013). However, typical day-time concentrations of sulfuric acid are too low to explain the nucleation rates observed in the atmosphere through binary nucleation of sulfuric acid and water (Kirkby et al., 2011). This gives rise to the assumption that organic vapors with low volatilities may play a bigger role in nucleation processes than previously assumed.

Earlier studies already reported nucleation processes without participation of sulfuric acid (Zhao et al., 2013; Gao et al., 2004), however, the possibility of contamination could not be excluded. In **Paper III**, we measured the cluster chemistry, thereby ruling out contamination by sulfuric acid (concentrations $<5 \times 10^4$ cm^{-3}). The APi-TOF detected protonated pyridine ($C_5H_5NH^+$) and nitrate (NO_3^-) as the dominant positive and negative ion, respectively, before adding any trace gases to the chamber.

We used alpha-pinene ($C_{10}H_{16}$), the most abundant monoterpene in the atmosphere, as a precursor for HOMs, by oxidizing it by exposure to ozone and hydroxyl radicals. The observed rate of HOM formation suggests that auto-oxidation was involved. We find that, in contrast to earlier studies investigating base-stabilized nucleation with ammonia or amines,

organic nucleation does not depend on the concentration of sulfuric acid. While we investigated pure organic nucleation first, we gradually added sulfur dioxide to the system afterwards, which left the observed nucleation rates largely unchanged ($[H_2SO_4] < 6 \times 10^6$ cm^{-3}).

We studied nucleation rates under three different ion concentrations: ion-free ('neutral'; J_n), galactic cosmic ray (J_{gcr}), and π^+ beam (J_π). These conditions correspond to cluster ion concentrations of roughly 0 cm^{-3}, 700 cm^{-3}, and 3000 cm^{-3}, allowing to study neutral nucleation and a range representative for the atmosphere between ground level and 15 km altitude. We observed a strong ion enhancement at HOM concentrations <1 pptv. At larger concentrations of HOMs the charge enhancement diminishes, as neutral nucleation rates keep increasing while ion-induced nucleation rates are limited by the ion pair production rate (Fig. 8). Dominant core ions were ammonium (NH_4^+), nitrate (NO_3^-), and negative HOM monomers (negatively charged clusters only containing C, H, and O). The observed ion enhancement of nucleation indicates that organic clusters are unstable without a charge, a result which is confirmed by quantum chemical calculation.

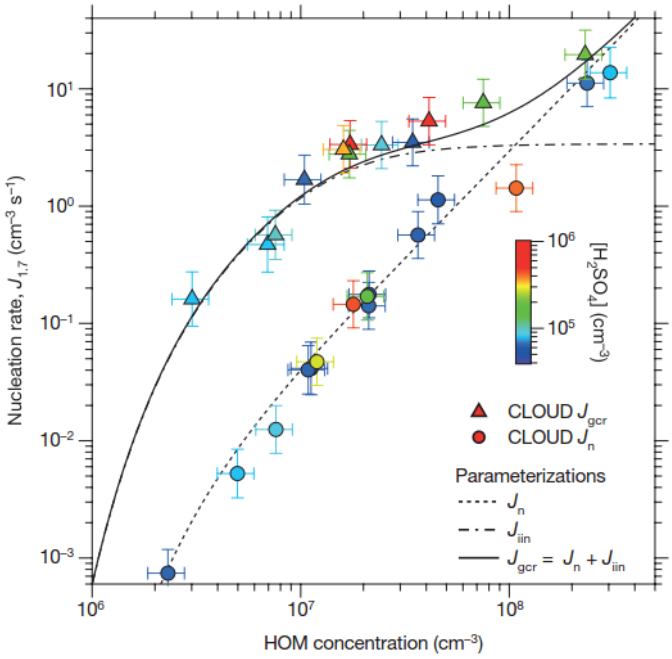

Figure 8. Nucleation rates versus concentration of HOMs. The color scale indicates the concentration of sulfuric acid. As nucleation rates increase, the charge effect diminishes. The figure was adopted from **Paper III**.

8.3 Governing factors for early growth of nuclei

Similar to nucleation rates, the growth rates observed in the atmosphere cannot be explained by sulfuric acid alone (e.g. Riipinen et al., 2012). It was assumed that HOMs play a significant role in condensational growth of nucleated particles, acting as the practically non-volatile condensable vapors that are necessary to describe atmospheric observations (Ehn et

al., 2014). However, the correlation has not been directly observed so far, and the condensing species were not identified. We investigated the influence of HOMs on size-segregated growth rates in **Paper IV**, by studying growth of organic particles in absence of inorganic acids and bases, such as sulfuric acid, ammonia, and amines. We covered a large range of sizes, observing the appearance of particles at mobility diameters 2–80 nm.

We found that growth rates did not depend on the concentration of sulfuric acid up to 10^7 cm^{-3}. In contrast, growth rates were strongly correlated to the concentration of HOMs (Fig. 9). While an ion enhancement was observed with organic nucleation (**Paper III**), charge did not influence organic particle growth. This can be explained through most HOM species in the chamber being neutral. However, due to experimental uncertainties, we cannot exclude an ion enhancement for cluster growth below 3 nm mobility diameter.

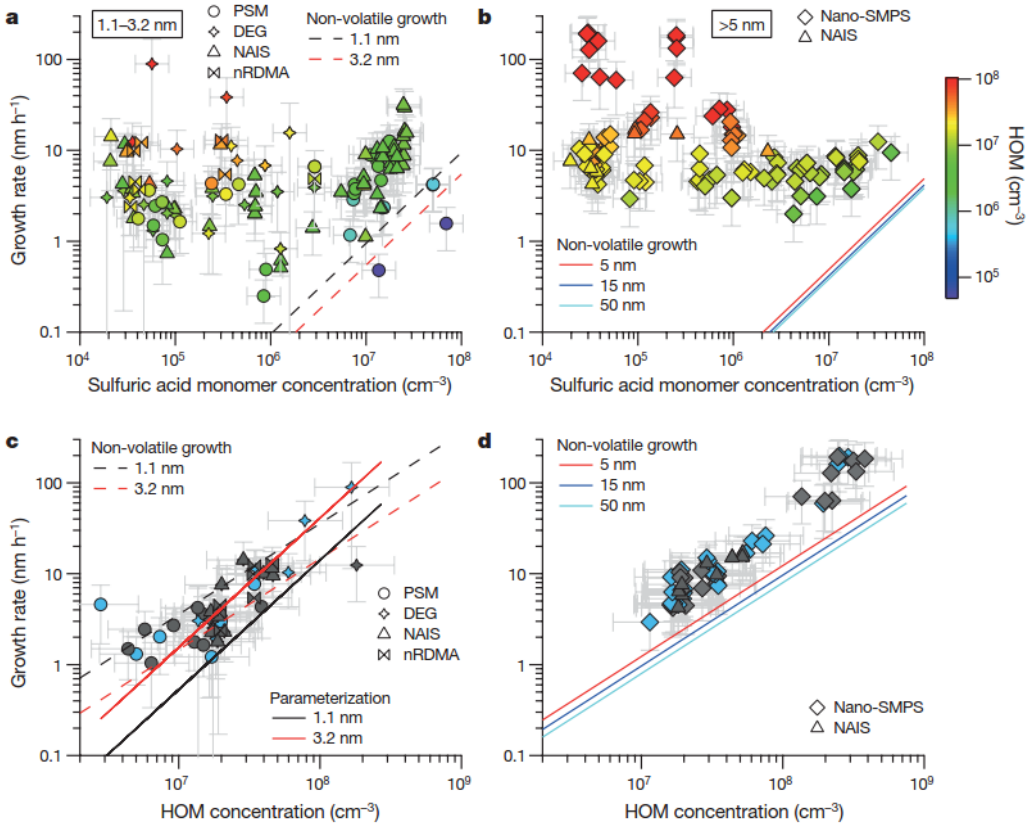

Figure 9. Growth rates versus concentrations of sulfuric acid (a, b) and HOMs (c, d). The figure was adopted from **Paper IV**.

To understand the mechanisms in more detail, a growth model was developed (**Paper IV**). The first attempt assumed non-volatile (collision-limited) HOM condensation. In this scenario, growth rates should decrease with increasing particle diameter, since the relative collision speeds decrease and the cross section becomes smaller. The experimental observations, however, indicate constant or slightly increasing growth rate towards larger particle sizes. This discrepancy indicates that HOM concentrations as measured with the CI-APi-TOF are not sufficient to explain observed growth rates. Since HOMs span over a wide

range of volatilities, as described in Sect. 8.1, it can be assumed that the measurement of HOMs, which relies on clustering with nitrate ions, is not efficient for organics with higher volatilities. We tested the growth model once again with increased concentrations of low-volatility organic compounds (LVOC), but the model results still did not match our observations. Finally, with including the curvature (Kelvin) effect in the growth model, the model results represented the measurements well.

In summary, while initial growth is driven by organic vapors of extremely low volatility (ELVOC), also more volatile vapors condense onto particles, once they have grown to larger sizes, and the Kelvin barrier has become insignificant.

8.4 Implications for the atmosphere

Drawing conclusions for the Earth's atmosphere from a very simplified version of it, as simulated in the CLOUD chamber, should be done with great caution. However, the mechanisms that are identified in laboratory experiments can increase understanding of atmospheric observations, or inspire future atmospheric measurements.

While there is no direct evidence of pure organic nucleation in the atmosphere (**Paper III**), it is possible that it contributes significantly in pristine environments such as tropical rain forests or over forested areas at high northern latitudes. A study at the high-altitude station Jungfraujoch, Switzerland, reported the observation of new-particle formation without sulfuric acid being involved (Bianchi et al., 2016), which is the atmospheric observation closest to pure organic nucleation so far. It is possible that nowadays pollutants are sufficiently well-mixed in the atmosphere, and therefore pure organic nucleation is unlikely to occur, even in remote environments. On the other hand, maybe the cleanest places on Earth have not been investigated yet. The possible influence of pure organic NPF on the pre-industrial climate was investigated through global modelling (Gordon et al., 2016), finding that the pre-industrial CCN concentrations could be higher, and thus the anthropogenic aerosol radiative forcing weaker than expected. However, at altitudes higher than 500 m, and in the present-day atmosphere in general, the influence of pure organic NPF on CCN concentrations is expected to be minor (Gordon et al., 2017).

The growth pattern can decide the fate of newly formed particles, influencing whether they will reach accumulation mode diameters, or be lost to pre-existing particles (or disintegrate). Since globally about half of cloud condensation nuclei (CCN) result from new-particle formation (Merikanto et al., 2009), it is likely that new insights on early nuclei growth (**Paper IV**) have an impact on the estimated CCN formation. A global aerosol model was used to estimate how CCN concentrations might change, when the condensation of low-volatility organic vapors is included. The results indicate that CCN concentrations are sensitive to the early nuclei growth. Model calculations with and without organic vapors taking part in early nuclei growth resulted in a factor of two difference in CCN concentrations (**Paper IV**).

However, a critical link to CCN are growth patterns, which might be different in the atmosphere due to differing volatility distributions and chemical properties of the available organic vapors.

9 Role of ions in new particle formation

Ion-induced nucleation is thought to be of minor importance in the atmosphere at ground level, with contributions around 10% to the total nucleation rate in the boreal forest (Manninen et al., 2009) and in most continental environments (Manninen et al., 2010). However, laboratory experiments suggest that ions might have a larger impact, as strong ion enhancement of new-particle formation rates were observed in a system involving sulfuric acid, ammonia, and water (Kirkby et al., 2011; Duplissy et al., 2016). Also with the pure organic nucleation mechanism discovered in **Paper III**, we observed a significant ion enhancement. So far, the total ion enhancement of new-particle formation was studied, by comparing measurements with and without ions being present in the chamber. In **Paper V** we go a step further, investigating the ion enhancement in more detail, studying dependencies on different trace gas concentrations, and separating the total ion enhancement in contributions from recombination and charged clusters.

By using a setup of nano-particle counters as described in Sect. 3.2, we were able to study the time evolution of the total particle population (N_{tot}) as well as the neutral fraction of it (N_{neu}) at the cut-off diameters 1.2 nm, 1.7 nm, and 2.2 nm. Furthermore, we used the high voltage clearing field to study ion-free conditions to determine rates of pure neutral nucleation. Those data combined gave us the opportunity to study the ion enhancement of new-particle formation in great detail. We calculated formation rates from both N_{tot} and N_{neu}, for conditions without and with ions present in the chamber. By using the scheme displayed in Figure 9, we calculated not only pure neutral new particle formation rates J_n, and ion-induced formation rates J_{iin}, but also the formation rate of particles which were charged but have recombined before detection J_{rec}, and the formation rate of charged particles $J_{\pm}$. We studied four systems of different chemical compositions including monoterpenes, sulfur dioxide, nitrogen oxides, and ammonia (Tab. 2).

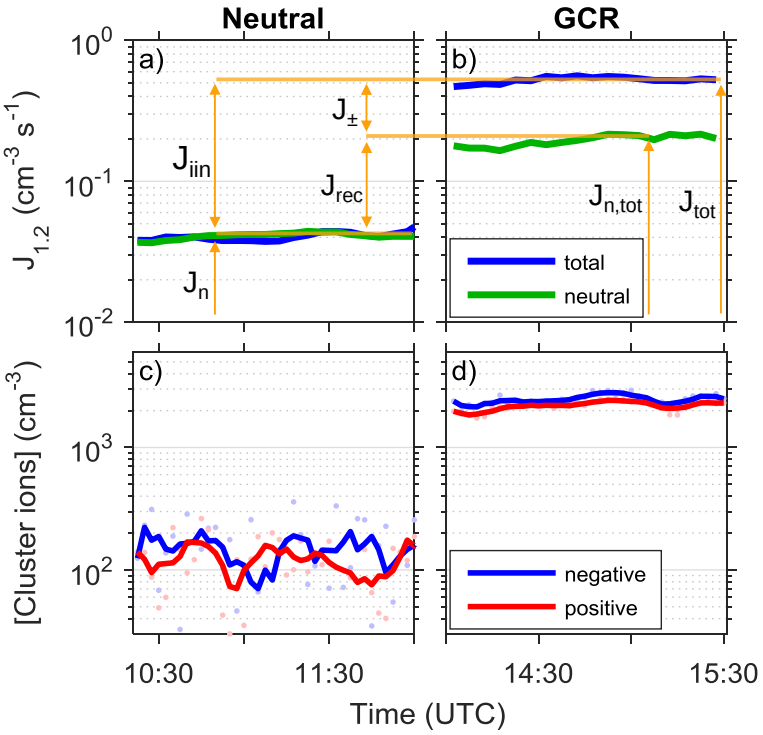

Figure 10. Example experiment to illustrate the scheme for calculating the different fractions of the total new-particle formation rate J_n, J_{rec}, $J_{\pm}$, and $J_{iin} = J_{rec} + J_{\pm}$. The figure was adopted from **Paper V**.

Table 2. Investigated chemical compositions when studying the influence of ions in NPF. The precursor vapors were added to the chamber together with ultra-pure synthetic air (N_2/O_2 = 79/21) at 38% relative humidity. The ozone mixing ratio was kept constant at 40 ppbv. The table was adopted from **Paper V**.

System no.	I	II	III	IV
Monoterpenes (MT)	✓	✓	✓	✓
Sulfur dioxide (SO_2)		✓	✓	✓
Nitrogen oxide (NO)			✓	✓
Ammonia (NH_3)				✓

We found that ions are most important for new-particle formation in conditions that are unfavorable for nucleation, e.g. at low concentrations of precursor vapors, when neutral molecular clusters are relatively unstable, and the charge is needed as a stabilizing agent. We observed this trend throughout the studied chemical compositions (system I–IV). Moreover, a larger fraction of charged particles was observed towards higher temperatures.

We compared our laboratory results to atmospheric measurements at the SMEAR II station at Hyytiälä, Finland (Hari and Kulmala, 2005). A similar temperature dependence of the

contribution of ions to new-particle formation was observed (Gagné et al., 2010). Furthermore, we noticed a significant difference in concentrations of small ions. While ionization rates in Hyytiälä (6–12 cm^{-3} s^{-1}; Laakso et al., 2004; Chen et al., 2016) are 3–6 times higher than at CLOUD (2 cm^{-3} s^{-1}), the concentration of small ions in Hyytiälä is about a factor of two lower than in the CLOUD chamber. The lower ion concentrations indicate the presence of an additional sink. We conducted experiments in the CLOUD chamber creating large condensation sinks, decreasing the ion concentration to levels similar to Hyytiälä. From those experiments we conclude that the additional sink in Hyytiälä is of the order 5×10^{-3} s^{-1}. Similar results were found in previous studies (Tammet et al., 2006; Hõrrak et al., 2008), the additional ion loss term was attributed to the forest canopy.

Our laboratory experiments indicate that the contribution of ion-induced nucleation decreases significantly towards lower concentrations of cluster ions (Fig. 11). This behavior can – at least partly – explain the discrepancy in contributions of ion-induced nucleation when comparing CLOUD laboratory results to atmospheric observations at Hyytiälä, Finland. Particularly, the effect of recombination is more significant at high ion concentrations.

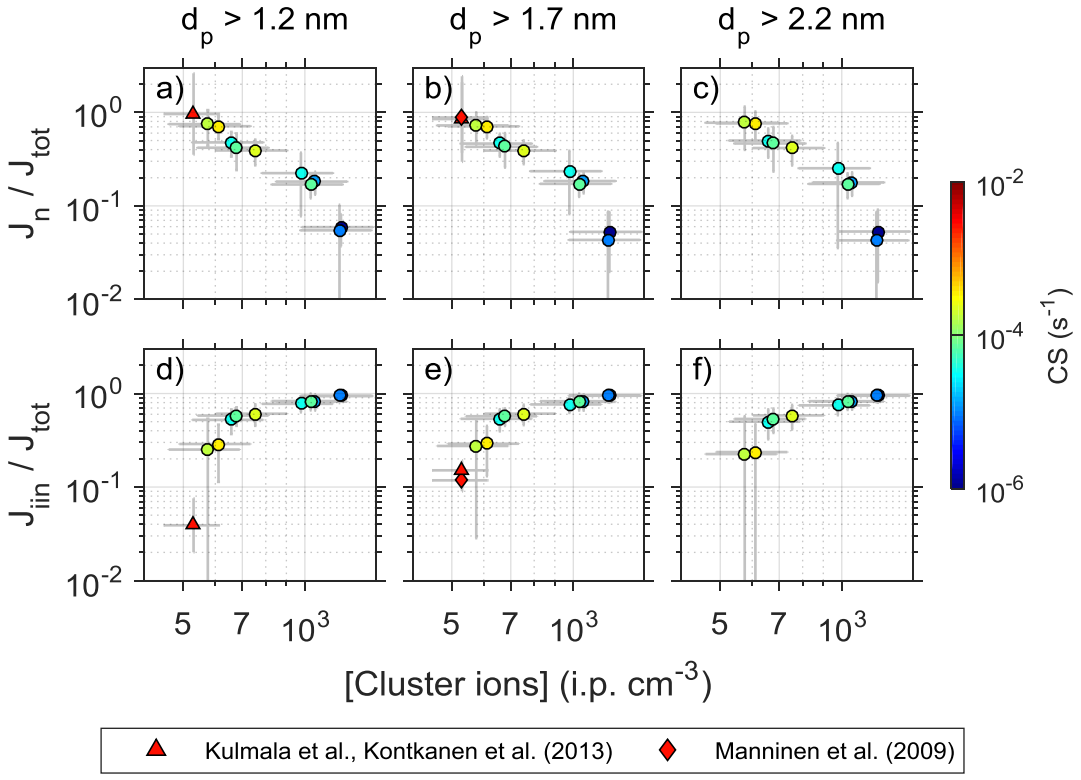

Figure 11. Contributions of neutral and ion-induced nucleation to new-particle formation at cut-off diameters 1.2 nm, 1.7 nm, and 2.2 nm. The color scale indicates the condensation sink. The figure was adopted from **Paper V**.

10 Review of papers and the author's contribution

Paper I addresses the concentration and size accuracy of the neutral cluster and air ion spectrometer and investigates inconsistencies in the data inversion routines. We measured counting efficiencies, tested five different inversion algorithms (inverters), and provided a procedure to achieve accurate measurements of ion concentrations. Whereas ion sizes were found to be accurate and independent of the inverter, ion concentrations were underestimated up to 30 % by three out of five inverters towards the lower end of the diameter range (roughly 1 nm). The other two inverters displayed inconsistent behavior. In this study, I conducted the calibration measurements, designed the dilution inlets, analyzed the data, and wrote the manuscript.

Paper II studies the influence of seasons and air mass origin on the bulk aerosol concentration, and on the aerosol chemical composition in central Vienna, Austria. We also investigated the factors governing new-particle formation in the urban environment. Our results suggest that the air mass origin influences the chemical composition of coarse aerosol, whereas fine aerosol chemical composition remains unaffected. Unless linked to meteorological behavior, air mass origin did not play a role in new-particle formation frequency. For this publication, I collected and processed number-size distribution data, classified new-particle formation events, and commented on the manuscript draft.

Paper III reports a new nucleation mechanism, involving organic precursor gases alone. New-particle formation was observed after adding alpha-pinene to the CLOUD chamber, a gas which subsequently reacted with ozone to form highly-oxidized molecules, many of which having very low volatilities. We found that ions significantly enhance this nucleation process at low concentrations of precursor vapors and nucleation rates well below the limiting ion pair production rate. For this research, I operated nano-particle counters and an ion spectrometer during the intensive measurement campaign, analyzed data from those instruments, participated in performing the experiments, and contributed in writing the manuscript.

Paper IV investigates the growth mechanisms of freshly formed clusters in the CLOUD chamber. We found that highly-oxidized molecules of extremely low volatility are responsible for initial cluster growth, whereas molecules of higher volatilities participate in condensational growth after they have overcome their maxima in the Nano-Köhler curve. A growth model was developed, which well represents the observed growth patterns. Global models indicate that the atmospheric concentration of cloud condensation nuclei is sensitive to early nuclei growth. In this study, I operated nano-particle counters and an ion spectrometer during the intensive measurement campaigns, analyzed data from those instruments and

calculated part of the growth rates that are reported in this publication, participated in performing the experiments, and contributed in writing the manuscript.

Paper V studies the role of ions in new-particle formation processes. We simulated four chemical environments in the CLOUD chamber, involving monoterpenes, sulfuric acid, nitrogen oxides, and ammonia. Our results indicate that charge, as stabilizing agent for molecular clusters, is most important in environments where neutral clusters are not thermodynamically stable; e.g. in a pure organic system at low precursor gas concentrations. Ion-induced nucleation was found to depend on the concentration of cluster ions, which is about a factor of two lower in the boreal forest at Hyytiälä, southern Finland, than at CLOUD. For this research, I operated nano-particle counters and an ion spectrometer during the intensive measurement campaign, analyzed data from those instruments including calculating nucleation rates, participated in performing the experiments, and wrote most of the manuscript.

11 Conclusions and outlook

New-particle formation and growth are in the focus of many research projects, since up to half of the globally available cloud condensation nuclei originate from secondary particle sources. Although nobody doubts that industrialization and anthropogenic emissions in general significantly changed and continue to change the atmosphere in terms of chemical composition and appearance, secondary particle formation cannot be explained by anthropogenic emissions alone. Therefore, in this thesis, we investigated natural influences on new particle formation, such as very low volatile organic vapors, or cosmic ray ionization, to better understand atmospheric observations.

Since one objective of this thesis is the study of ion-effects in new-particle formation (*objective iii*), enabling a precise measurement of ion spectra is crucial (*objective i)*. The accuracy of the ion size and concentration response of a widely used ion spectrometer, neutral cluster and air ion spectrometer (NAIS), was investigated with focus on the data inversion routine (**Paper I**). It was confirmed that the NAIS measures ion sizes with great precision, especially at small diameters (< 5 nm). However, concentration values deviate up to 30% from reference values and the result strongly depends on the version of the data inversion routine. By using the recommended inversion routines and the counting efficiency functions determined in this thesis, ion concentrations can be determined at uncertainties lower than 10% (*objective i*).

In an urban environment at Vienna, Austria, most fine particles originate from regional sources, one of which being new-particle formation. In contrast, coarse aerosol particles are influenced by the origin of the air mass, which, depending on meteorological conditions, can be thousands of kilometers away (**Paper II**). The results also indicate the importance of photochemistry for new-particle formation. Since OH and consequently ozone formation are promoted by UV radiation, oxidation processes are enhanced on sunny days, which in turn increases the formation of low-volatility organic vapors (Ehn et al., 2014).

These low volatility organics influence nucleation processes, and sulfuric acid, which has been seen as critical ingredient for new-particle formation, turned out not to be necessary for nucleation (**Paper III**; *objective ii*). By measuring the molecular composition, contamination could be ruled out. Furthermore, organic nucleation rates are largely independent of sulfuric acid concentrations ($< 6 \times 10^6$ cm^{-3}). At low concentrations of HOMs and nucleation rates well below the ion pair production rate, ions significantly enhance pure organic nucleation (*objective iii*).

Low volatility organic vapors also influence early growth of organic particles (**Paper IV**). While gases with extremely low volatility are the key player in nucleation and initial growth, gases with higher volatilities also start to condense on the cluster when it has grown to larger sizes, and the Köhler maximum was overcome. A growth model was developed, which well represents the observed processes (*objective ii*). The observed particle growth can only be explained with larger concentrations of molecules with higher volatilities. Therefore, our

data indicates that the CI-APi-TOF mass spectrometer detects molecules with higher volatilities inefficiently, leading to underestimated concentrations of those compounds. Consequently, also atmospheric concentrations of LVOCs (low-volatile) or SVOCs (semi-volatile) could be higher than currently expected. Further instrumental development is needed to study LVOCs and SVOCs, as well as their influence on new-particle formation in more detail.

Ions are known to stabilize molecular clusters by reducing evaporation rates (Yu and Turco, 2001), thus ions can assist in new-particle formation as often observed in chamber and ambient studies (e.g. **Paper V**; Manninen et al., 2009). However, atmospheric observations suggest only minor contribution of ion-induced nucleation, at least in the boundary layer. To tackle *objective iii*, we investigated the contributions of ion-induced nucleation as well as contributions of recombination in four systems of different chemical compositions (from pure organic to a simulations of the boreal forest in Finland; see Table 2 for details). Ion-induced nucleation contributes most when neutral clusters are relatively unstable, e.g. when the concentration of precursor vapors is low, and thus the charge is needed for a cluster to be stable. With increasing concentration of condensable vapors, as well as with increasing number of components in the chemical system, the contribution of ion-induced nucleation decreased. When simulating an environment similar to the boreal forest at the SMEAR II measurement station at Hyytiälä, southern Finland, the contribution of ion-induced nucleation was sensitive to the concentration of cluster ions in the chamber. At the SMEAR II station, the concentration of cluster ions is about 50% lower than at CLOUD, even though ionization rates are a factor of 3–6 higher. This implies that an efficient sink for ions and charged clusters is present in the boreal forest at SMEAR II. This difference in cluster ion concentrations and its implications (e.g. difference in recombination rate) may explain the discrepancy when comparing the contributions of ion-induced nucleation at CLOUD and at SMEAR II (*objective iii*). Apparently, the ion balance at CLOUD is not representative for the boreal forest environment. Only when an additional sink from accumulation mode particles is present in the CLOUD chamber, and the concentration of cluster ions has decreased to levels similar to the boreal forest, the contribution of ion-induced nucleation from chamber and atmospheric measurements is comparable (**Paper V**). Further investigation is needed to understand the ion balance in more detail both at CLOUD and in the boreal forest, which will help to better understand the influence of ions in nucleation processes.

The processes investigated in this thesis are all closely coupled to a big source of cloud condensation nuclei: new-particle formation. Aerosol particles and clouds significantly shape the Earth's atmosphere, especially its radiation balance, and are thus an important part when estimating the development of the global climate. Since our climate reacts to changes with a certain delay, it is crucial to be able to predict the consequences for the future of our current actions and policies. Currently, radiative forcing of aerosol particles and especially aerosol-cloud interactions still have large error bars (IPCC, 2013). This thesis is one of many steps towards reducing those error bars, which will make decision and policy making a lot easier.

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